BE IT KNOWN, that I, Dennis J. O'Rear, a citizen of the United States of America, and resident of the City of Petaluma, State of California, I, Steven S. Mathur, a citizen of the United States of America, and a resident of the City of Danville, State of California, I, Thomas Van Harris, a citizen of the United States of America, and a resident of the City of Benicia, County of Solano, State of California, I, Curtis Munson, a citizen of the United States of America, and a resident of the City of Oakland, State of California, and I, Cong-Yan Chen, a citizen of China, and resident of the City of Kensington, State of California have invented new and useful improvements in

MANUFACTURE OF HIGH OCTANE ALKYLATE

MANUFACTURE OF HIGH OCTANE ALKYLATE

CROSS REFERENCE TO RELATED APPLICATIONS

The present application is related to application Serial Number _____ (Attorney Docket No. 005950-724), filed concurrently herewith, entitled

5   PREPARATION OF HIGH OCTANE ALKYLATE FROM FISCHER-TROPSCH OLEFINS. The disclosure of said related application is incorporated herein in its entirety.

BACKGROUND OF THE INVENTION

Field of the Invention

10   The present invention relates generally to a process for converting Fischer-Tropsch olefin-containing light fractions into high octane alkylates. More particularly, this invention relates to a process of using a catalytic dehydration/isomerization reaction to convert Fischer-Tropsch light olefin fractions into feeds for alkylation.

15   Description of Related Art

Because of their high octane numbers and low vapor pressures, alkylates have been used for many years as blending components in motor gasolines. The alkylation process involves the reaction of light olefins such as propylene and butylene with isoparaffins such as isobutane and isopentane in the presence of an

20   acid catalyst such as H_2SO_4 and HF to form highly branched, isoparaffinic products known as alkylates. Typical sources for light olefins include catalytic crackers, cokers and vis-breakers.

The Fischer-Tropsch process also produces light olefins. The process involves reacting synthesis gas composed mainly of CO and H_2 in the presence of a

25   suitable catalyst to form a variety of predominantly linear hydrocarbonaceous

solid, liquid and gaseous products. Some of these products can be refined using known procedures such as hydrotreating, hydrocracking and hydroisomerization to yield moderately branched, isoparaffin-rich middle distillate fuels such as diesel and jet fuels. A gaseous phase produced in a Fischer-Tropsch synthesis, upon condensation and subsequent distillation, produces a light olefin product composed primarily of C_3-C_4 olefins. However, this product is considered to be poorly suited for use as a feedstock for conversion to alkylates for a number of reasons.

Products of Fischer-Tropsch syntheses normally contain relatively high levels of oxygenates, frequently in amounts above 4000 ppm oxygen. Oxygenates can react to form water which would dilute acid catalysts conventionally used in alkylation. Accordingly, light olefin feedstocks for alkylation should contain no more than 4000 ppm oxygenates, preferably much less. Also, light olefin streams from Fischer-Tropsch processes have relatively low levels of isobutane. As such, they do not constitute a good source for isobutane. In the alkylation process, isobutane feedstocks should contain at least 30% by weight, preferably up to 75% by weight isobutane. Also, Fischer-Tropsch light olefin streams are composed predominantly of 1-butene. It has been observed that 1-butene tends to give alkylates with lower octane numbers than 2-butene. Desirably, the ratio of 2-butene to total butenes in the feed for alkylation should be at least 0.1 and most preferably at least 0.5.

Hydroisomerization processes have been used to produce moderately branched isoparaffins in the distillate fuel boiling range. However, they cannot be used to produce high-octane, highly branched isoparaffins in the gasoline boiling range. If hydroisomerization processes are run in a severe mode in an attempt to create highly branched products instead of moderately branched products, the feedstock cracks to form excessive amounts of undesirable light gases. Accordingly, the only practical method to manufacture high octane, highly branched, gasoline boiling range isoparaffins is by alkylation.

Consideration has been given to converting Fischer-Tropsch C_3-C_4 olefin streams into a feedstock suitable for alkylation by total hydrogenation or by using known treatments to lower the oxygenate content to an acceptable level. However, these approaches would necessitate a separate step to isomerize butane while

5   hydrogenation would saturate the olefins in the C_4 stream. Also, the oxygenates removed from the C_3-C_4 stream would not be converted into alkylates. What is needed is an economical process for converting a C_3-C_4 light olefin fraction from a Fischer-Tropsch process into a highly branched isoparaffin alkylate suitable as a blending component to prepare high octane gasolines.

10   Alkylation using light olefins obtained via a Fischer-Tropsch synthesis are described in U.S. Patent Nos. 4,279,830; 4,046,830; and 4,049,741. These patents do not disclose using a combined dehydration/isomerization process to reduce oxygenate levels and increase the amount of olefins and 2-butene.

It is an object of the invention to provide a process for economically

15   preparing high octane alkylates from a Fischer-Tropsch C_3-C_4 light olefin stream.

It is another object of the invention to utilize a Fischer-Tropsch C_3-C_4 olefin fraction and an isobutane stream obtained by hydrocracking a Fischer-Tropsch 300°F+ product to produce a high octane alkylate.

These and other objects of the present invention will become apparent to

20   the skilled artisan upon a review of the following description, the claims appended hereto and the Figure of the drawing.

SUMMARY OF THE INVENTION

The objectives of the invention are attained by a process which includes the following steps:

25   (a)   recovering a light C_3-C_4 olefin product stream from a Fischer-Tropsch reactor;

(b)   contacting the olefin stream with a dehydrating/isomerizing catalyst to dehydrate oxygenates in the olefin stream to form additional olefins and also convert 1-butenes to 2-butenes;

(c)   hydrocracking a C_5+ product from a Fischer-Tropsch

5   synthesis to generate an isobutane-containing stream;

(d)   blending the product stream from step (b) which contains less than about 4000 ppm oxygenate, with the product stream from step (c);

(e)   alkylating the blend of step (d); and

10   (f)   recovering a highly branched, isoparaffinic alkylate having a research octane number greater than 80.

A key feature of the invention lies in the discovery that certain dehydration catalysts can serve a dual function. On the one hand, they dehydrate linear alcohols present in the C_3-C_4 olefin stream (e.g., 1-propanol and 1-butanol) to

15 provide additional C_3 and C_4 olefins (which also reduces the amount of oxygenates present in the feedstock), and on the other hand, they isomerize 1-butenes to 2-butenes which can increase the octane value. Since the C_3-C_4 olefin feed used in the alkylation stage should contain no more than about 4000 ppm oxygenate and preferably less than 1000 ppm, it is desirable to treat the C_3-C_4 olefin stream to

20 remove at least a portion of organic acids present and at least a portion of the alcohols which have not been dehydrated. Suitable known techniques to accomplish this include extractive or azeotropic distillation, decarboxylation, adsorption and water extraction or water washing.

BRIEF DESCRIPTION OF THE FIGURE OF THE DRAWING

25   The Figure is a schematic flow diagram of one embodiment of the invention.

DETAILED DESCRIPTION OF PREFERRED
EMBODIMENTS OF THE INVENTION

The present invention uses products obtained from a Fischer-Tropsch synthesis to prepare alkylates having a research octane number of at least 80,

5   preferably at least 85 and most preferably at least 90. As indicated earlier, the Fischer-Tropsch synthesis generally involves reacting a syngas composed primarily of CO and H_2 in the presence of a catalyst under suitable temperatures and pressures to yield a variety of gaseous, liquid and solid products composed primarily of hydrocarbonaceous materials. Any source of hydrocarbon can be

10   used to generate the syngas including: natural gas, coal and petroleum products. The reaction can be conducted in a variety of reactors including fixed bed reactors, slurry reactors, fluidized bed reactors or a combination of different types of reactors. Typical reaction conditions include temperatures ranging from about 300°-700°F, pressures ranging from about 10-600 psia and catalyst space

15   velocities ranging from about 100-10000 cc/g/hr. Mole ratios of hydrogen to carbon monoxide may range from about 0.5-4. Suitable catalysts include one or more Group VIII catalytic metals such as Fe, Ni, Co, Ru, and Re. An example of a typical Fischer-Tropsch catalyst comprises Co and one or more of Re, Ru, Fe, Ni, Th, Zr, Hf, U, Mg and La on a suitable inorganic support.

20   The effluent stream from the Fischer-Tropsch reactor is processed to recover a light olefin stream. A wide variety of products is generated in a Fischer-Tropsch synthesis. These include a gaseous phase and a liquid waxy phase. The gaseous phase is cooled in a separation zone to condense the hydrocarbons. Unreacted syngas is recycled back to the Fischer-Tropsch reactor. Water present

25   in the condensate is removed by using known techniques, for example by density differences. The condensate alone or admixed with the waxy phase is forwarded to a distillation zone.

As indicated, the Fischer-Tropsch process generates a wide range of generally linear hydrocarbonaceous products. The atmospheric boiling point of some of these products is shown below.

Compound	Boiling point at atmospheric pressure, °C / °F
Carbon monoxide	-191 / -312
Carbon dioxide	-78 / -61 (solid)
Propylene	-48 / -54
Propane	-42 / -44
1-butene	-6 / 21
n-Butane	-0.5 / 31
n-Pentane	36 / 97
Oxygenates:	
Methanol	39 / 102
Ethanol	78 / 172
1-propanol	97 / 207
1-butanol	117 / 243
Acetic Acid	118 / 244
Propanoic Acid	144 / 291
Butanoic acid	164 / 327

It is evident that a C_3 and/or C_4 fraction can be obtained from this effluent by distillation. The cut point of the distillation should be high enough to include butenes, but low enough to exclude traces of methanol. This means that the end point of the C_3-C_4 fraction should be between -6 and 39°C, preferably between 0 and 30°C, most preferably between 10 and 20°C. Simple distillation may not be effective in generating a C_3-C_4 fraction having an oxygenate content below 4000 ppm as azeotropes may be formed. If the oxygenate content is still in excess of 4000 ppm after simple distillation, other techniques may be used to lower the oxygenate content including azeotropic distillation, extractive distillation, water washing or combinations thereof. It should be understood that the oxygen is present as oxygenates and that oxygenate contents are on a water-free and air-free

basis. The term "oxygenates" as used herein refers to any carbon and oxygen-containing hydrocarbon compound. Examples of oxygenates include alcohols, acids, aldehydes, esters, ketones and the like.

The boiling range of a C_3-C_4 fraction may be suitably determined using an
5   ASTM D2887 procedure, taking appropriate precautions to prevent evaporation of the sample prior to analysis. Preferably the concentration of methanol can be determined by a GC analysis of the feed with suitable calibration for oxygenates.

In extractive distillation, an additional component is added to facilitate the separation. This mass-separating agent, or solvent, is fed into the distillation
10   column near the top. Typically, the solvent has a low volatility and exerts a selective attraction for the oxygen-containing contaminants. This attraction results in an increased separation factor. The low solvent volatility insures that significant amounts of the solvent, typically 60 to 90 percent, are found on every stage or tray in the column. Solvent loaded with the oxygen contaminant is removed at the
15   bottom of the distillation tower and regenerated separately, by another distillation. An example of such a system is the separation of isobutane from butene using furfural as a solvent. For the removal of oxygenates from the Fischer-Tropsch liquids listed above, suitable solvents include high molecular weight carboxylic acids (e.g. neodecanoic acid and 2-ethyl-hexanoic acid) and alcohols such as
20   octanol, 2-ethyl hexanol and decanol. Ionic liquids may be used for the removal of alcohols and acids. High molecular weight bases such as organic amines may be used to remove carboxylic acids. A further description of Extractive Distillation can be found in Chemical Engineers' Handbook, John. H. Perry, 4th Edition, Section 13 pages 46-55, incorporated herein by reference.

25   In azeotropic distillation an additional solvent is added. In this case the solvent selected forms a minimum boiling azeotrope with the contaminants. The azeotropic mix boils at a lower temperature than the other components and is carried overhead in the distillation column with the oxygen-free product going to bottoms. An industrial example of azeotropic distillation is the separation of

ethanol from water using benzene. In an example, 11% water and 89% ethanol are fed to a distillation column and benzene added near the top of the column. Water -benzene - alcohol in a near azeotropic composition (22-54-24% respectively) are removed at the top of the column and pure ethanol is removed at

5   the bottoms. The benzene is recovered by condensing the overhead vapor and allowing the immiscible benzene / water phase to split. Benzene (with some water and alcohol) is fed back to the column, and the water phase (containing some benzene and alcohol) further purified with additional distillation. For the removal of alcohols from Fischer-Tropsch liquids, suitable solvents include those solvents

10   known to form azeotropic mixtures with the alcohol alone. For 1-propanol, these include dioxane, butyl formate, chlorobenzene, fluorobenzene, all isomers of xylene, toluene, methyl cyclohexane, and the like. A further description of Azeotropic Distillation can be found in Chemical Engineers' Handbook, John. H. Perry, 4th Edition, Section 13 pages 46-55, the disclosure of which is incorporated

15   herein.

        In addition to the propylene and butene in the C_3-C_4 fraction, a considerable amount of alcohols are present in the higher boiling range fractions. These alcohols are predominantly linear alcohols. They have good research octane values, but moderate motor octane values: n-propanol octane numbers are 117

20   research and 90 motor, n-butanol octane numbers are 95 research and 79 motor. Alcohols in this range normally retain water. When these alcohols are added to gasolines, the water will be absorbed into the gasoline and form a haze upon cooling. While in some situations the alcohols can be left in the naphtha product, it is a feature of the present invention to convert these alcohols into additional

25   propylene and butenes by dehydration.

        Products obtained from the distillation zone include a light gaseous product composed primarily of methane and ethane, a C_3-C_4 olefin-containing stream, a C_5-300°F product and a 300°F+ product. Prior to forwarding the C_3-C_4 olefin stream to the dehydration/isomerization zone, the olefin stream may be further

treated to lower the oxygenate level. It is an important feature of the invention that the amount of oxygenate in the C_3-C_4 olefin stream when it is admixed with the isobutane stream for alkylation, should be no more than 4000 ppm, preferably not more than 2500 ppm, and most preferably, 1000 ppm or below. If the C_3-C_4

5   olefin stream leaving the dehydration/isomerization zone has an oxygenate content above the 4000 ppm limit, the stream should be further processed to reduce the oxygenate content.

The oxygenates can be measured by GC-MS or simple GC. GC-MS is preferred. While the oxygen concentration is given in terms of oxygenates, it may

10   also be given in terms of oxygen concentration. A limit of no more than 4000 ppm oxygenates, more preferably no more than 1000 ppm oxygenates, refers to the olefin stream. If the olefin stream is diluted with other streams, e.g., isobutane, the oxygenate determination is adjusted to account for the dilution, and is always expressed as a concentration of the olefin stream component above.

15   The dehydration of alcohols to form olefins is a well-known chemical operation and representative methods have been described in the patent literature. U.S. Patents 4,398,050, 4,547,601 and 4,260,841 disclose methods for dehydrating alcohols obtained in a Fischer-Tropsch synthesis. The disclosures of these patents are incorporated herein by reference. The preferred catalyst

20   disclosed in the '050 patent for dehydration of alcohols is alkalized to prevent condensation and polymerization of the olefins. This patent does not discuss simultaneous olefin isomerization during the course of the dehydration reaction. While catalysts of this type are suitable for alcohol dehydration, some may not simultaneously isomerize 1-butene in the feed (including 1-butene produced from

25   the alcohol dehydration) to 2-butene. Catalysts preferred in this invention are not alkalized completely, and contain at least some acidity. Catalysts may comprise any of the following: alumina, silica-alumina, zeolites, clays, etc. The key feature to selecting a suitable catalyst is that during the dehydration of a mixture that contains both alcohols and 1-butene, a product is obtained that contains less than

4000 ppm oxygenate while at least 10% of the 1-butene is converted into 2-butene, preferably at least 30% and most preferably at least 50%.

Dehydration catalysts preferred for this invention can be identified by simple experiments using pure 1-butanol in small laboratory down-low units operated at atmospheric pressure and 1.0 LSHV with 0.2-0.4 grams of catalyst. The catalyst temperature is adjusted over the temperature range of about 300°-600°F to achieve 90% 1-butanol conversion, if possible. If measurements at precisely 90% are not generated, the results may be interpolated by a plot of the variables versus butanol conversion.

Examples of suitable catalysts are shown below.

	Broad	Preferred	Most Preferred
Temperature for 90% 1-Butanol Conversion, °F	300-600°	300-600°	300-600°
2-Butene content as % of total butenes	>10	>50	>75
Selectivity of Butanol conversion to butenes	>50	>50	>90
Catalyst	Alumina	Zeolites (ZSM-5,Y Zeolite)	1-Dimensional 10-ring Zeolites (SSZ-32)

An important feature of these catalysts is the ability to suppress formation of C_5+ olefins. C_5+ olefins are formed if the catalyst is too acidic or has a structure that consists of 12-ring intersecting 10-ring pores. C_5+ olefins have high octane and are not necessarily detrimental to the production of high octane gasoline blending streams; however, they have some undesirable features, and it is preferred to limit their formation. These undesirable features include increased air pollution during gasoline use, increased tendency to form oxidized products (gums) during gasoline storage, and reduced ability to form the desired high octane, highly branched isoparaffinic alkylate. Another desirable feature of these

catalysts is that they is that they suppress the saturation of olefins to form paraffins. The C_4 olefins can be saturated to form paraffins if hydrogen is present along with the feedstock. These paraffins will be normal paraffins and not suitable for alkylation. Catalysts which have high selectivities to the desired butene products (>90%) naturally have low selectivities to formation of other products such as C_5+ olefins and paraffins.

The most preferred class of catalyst are those that contain only 10-ring pores arranged in 1-dimension. Zeolites can be identified by determining their crystal structure by known methods. Zeolites are summarized in "Atlas of Zeolite Structure Types" prepared by the International Zeolite Association. Examples of structures (and common names) of zeolites and crystalline aluminophosphates of this type include: AEL (SM-3, SAPO-11), AFO (SAPO-41), EUO (EU-1), MTT (ZSM-23, SSZ-32), SFF (SSZ-44), STF (SSZ-35), TON (Theta-1, ZSM-22, SSZ-20). Other zeolites with structures not officially recognized but likely to be 1-D 10-ring pores include: ZSM-48, SUZ-4, IM-5, NU-88, SSZ-57, and ZSM-25. Of this list, MTT, TON and ZSM-48 are most highly preferred.

The following batch reactor technique was employed to identify catalysts useful for conversion of 1-butanol into butenes, preferably 2-butene.

For each experiment, 1.0 g of catalyst was charged to a 25 mL stainless steel pressure batch reactor equipped with a magnetic stirring bar. The reactor was evacuated and backfilled with nitrogen several times. While under nitrogen, 5 mL of 1-butanol was added. The reactor was then heated with stirring for 18 hours at 200°C. Upon heating, the pressure rose to approximately 90-150 psig. At the end of the heating period, the reactor was cooled to room temperature and then to dry ice temperature. Through a rubber septum 5 mL of n-hexane was added. Next ~2 g of n-heptane was accurately weighed in to serve as an internal standard. The product was then removed from the reactor and analyzed by gas chromatography.

Samples of various acidic catalysts were evaluated in this batch test with the following results:

Catalyst Identification	Zeolite Ring Aperture Size	Pore Dimensionality	Alpha Value	1-Butanol conversion, %	Butene selectivity, %
CBV-760 Y zeolite	12	3	28	77.9	5.6
CBV-9010 Y zeolite	12	3	3	83.3	9.5
Al_2O_3-bound SSZ-32	10	1	~300	44.6	55.2
Al_2O_3-bound ZSM-5	10	3	300	91.8	43.6

The preferred catalysts for this application will have the highest possible values for 1-butanol conversion and selectivity for formation of butenes. The catalysts will have conversions and selectivities under conditions of this test equal to or greater than 25%, preferably equal to or greater than 40%, and most preferably equal to or greater than 75%. From this data, the preferred catalysts appear to be zeolites 10-ring apertures, and most preferably those with 1 - dimensional pores.

The following flow micro reactor tests were employed to identify catalysts suitable for conversion of alcohols into olefins.

A flow-type microunit was equipped with a stainless steel fixed bed reactor and an on-line GC.

The catalysts studied here are as follows:

1. Alumina-bound Al-SSZ-32

2. Alumina-bound Al-ZSM-5

3. Alumina base (Condea Chemie, #20.301/90, as-provided by the supplier)

4. Alumina base (calcined in air at 950 °F for 4 hours).

The catalysts (0.24-0.26 g = 4.0 cc each) were crushed to 24-60 mesh and, prior to the reaction, dehydrated in a N_2 flow (200 cc/min) at 662°F (350°C) overnight.

The reactions were carried out in a down-flow mode at atmospheric

5   pressure and 0.5/1.0 LHSV between 392° and 572°F. In one case (Al-SSZ-32), the reaction was carried out at 240 psig. No carrier gas such as H_2, N_2 or He was used during the reaction.

The products were analyzed with an on-line GC using a HP-1 capillary column and a FID. The FID Response Factors (RF) for 1-butanol, di-n-butyl ether

10   and hydrocarbons were determined assuming hydrocarbon RF = 1.

Component	Response Factor (RF)
1-butanol	1.4663
di-n-butyl ether	1.2626
octane (as internal standard)	1.0000

15   The response factors are defined so that:

Wi = Woctane x (Ai/Aoctane) x (RFi/RFoctane)

where Wi stands for the weight of component i, Ai for the GC area of component i and RFi for the Response Factor of component i with RFoctane = 1 for the internal standard octane.

Results from 1-butanol dehydration over alumina bound Al-SSZ-32:

Temperature, °F	482	482	482	392	410	410
Pressure, psig	0	0	0	0	0	240
LHSV, h-1	0.5	1.0	2.0	1.0	1.0	1.0
1-Butanol Conversion, %	100	100	100	7.7	24.8	17.9
Yield, wt%						
1-Butene	13.3	15.2	15.2	1.5	5.2	1.4
cis-2-Butene	24.0	30.7	31.5	1.8	6.2	3.3
trans-2-Butene	40.4	50.4	51.5	3.0	10.7	5.6
iso-Butene	0.9	0.5	0.5	0.1	0.1	0.1
Total Butenes	78.6	96.8	98.7	6.3	22.2	10.4
Other products	21.4	3.2	1.3	1.4	2.6	7.5
Selectivity, wt%						
1-Butene	13.3	15.2	15.2	19.1	21.0	7.8
cis-2-Butene	24.0	30.7	31.5	22.9	25.0	18.4
trans-2-Butene	40.4	50.4	51.5	38.5	43.2	31.3
iso-Butene	0.9	0.5	0.5	1.3	0.4	0.5
Total Butenes	78.6	96.8	98.7	81.8	89.6	58.0
Other Products	21.4	3.2	1.3	18.2	10.5	41.9

These results show that the 1-dimensional 10-ring zeolite SSZ-32 gives conversions of 100% and selectivities to butenes of over 95%. Furthermore, the content of 2-butenes in the butene fraction is high and near equilibrium. Also, the content of iso-butene is low possibly due to the confined nature of the pores in this catalyst. Operation at pressures near atmospheric pressure is preferred since this gives the maximum selectivity to the desired butenes. In commercial practice, operation at exactly atmospheric pressure is not practical, but the pressure should be as low as possible, preferably below 100 psig, more preferably below 50 psig, and most preferably below 25 psig.

Results from 1-butanol dehydration over alumina bound Al-ZSM-5:

Temperature, °F	482	392	392	410
Pressure, psig	0	0	0	0
LHSV, h-1	0.5	0.5	1.0	1.0
1-Butanol Conversion, %	100	35.9	22.8	35.4
Yield, wt%				
1-Butene	11.9	4.7	4.0	4.8
cis-2-Butene	22.1	4.9	3.1	4.9
trans-2-Butene	36.3	7.4	4.8	7.2
iso-Butene	0.5	0.2	0.1	0.1
Total Butenes	70.8	17.2	12.0	17.0
Other products	29.2	18.7	10.8	18.4
Selectivity, wt%				
1-Butene	11.9	13.1	17.5	13.6
cis-2-Butene	22.1	13.7	13.6	13.8
trans-2-Butene	36.3	20.6	21.1	20.3
iso-Butene	0.5	0.6	0.4	0.3
Total Butenes	70.8	48.0	52.6	48.0
Other Products	29.2	52.1	47.4	52.0

In comparison to the 1-dimensional 10-ring zeolite SSZ-32, results using the 3-dimensional 10-ring zeolite ZSM-5 show poorer selectivities to the desired butene products. Thus, while it can be used, it is not a preferred catalyst.

Results from 1-butanol dehydration over a solid oxide alumina:

Temperature, °F	482	482	572
Pressure, psig	~0	~0	~0
LHSV, hr^{-1}	1.0	0.5	0.5
1-Butanol Conversion, %	15.9	18.6	85.1
Yield, wt%			
1-Butene	1.4	2.2	67.3
cis-2-Butene	0.1	0.1	0.5
trans-2-Butene	0.1	0.1	1.7
iso-Butene	0	0	0.1
Total Butenes	1.6	2.4	69.6
Other products	14.3	16.3	15.5
Selectivity, wt%			
1-Butene	8.8	11.7	79.1
cis-2-Butene	0.6	0.4	0.6
trans-2-Butene	0.6	0.4	2.0
iso-Butene	0	0	0.1
Total Butenes	10.0	12.5	81.8
Other Products	90.0	87.5	18.2

In comparison to the more acidic zeolites, alumina was less active and required higher temperatures to achieve conversions above 80%. In addition, the primary product from the dehydration of 1 -butanol is 1-butene, which gives an inferior alkylate product in comparison to 2-butene. Thus, while alumina can be used as a dehydration catalyst, it is not the material of choice.

Results from 1-butanol dehydration over alumina (calcined) :

Temperature, °F	482	482	572
Pressure, psig	~0	~0	0
LHSV, hr^{-1}	1.0	0.5	0.5
1-Butanol Conversion, %	41.7	54.0	100
Yield, wt%			
1-Butene	10.0	13.4	80.5
cis-2-Butene	0.1	0.2	5.6
trans-2-Butene	0.2	0.2	13.8
iso-Butene	0	0	0.1
Total Butenes	10.3	13.8	100.0
Other products	31.4	40.2	0
Selectivity, wt%			
1-Butene	24.0	24.8	80.5
cis-2-Butene	0.2	0.4	5.6
trans-2-Butene	0.5	0.4	13.8
iso-Butene	0	0	0
Total Butenes	24.7	25.6	100.0
Other Products	75.3	74.4	0

Calcining the alumina prior to use increased its activity significantly. When operated at near 100% conversion of 1-butanol, selectivity to butenes was excellent. However, the predominant butene was again 1-butene and not the preferred 2-butenes. Thus, if alumina is used as the dehydration catalyst, it preferably should be calcined prior to use.

In addition to these requirements, the isomerization-dehydration catalyst must be water-tolerant. Weakly acidic silica-alumina may be a suitable isomerization-dehydration catalyst but chlorided and/or fluorided catalysts would

not be suitable since the halogens will be removed from the catalyst during reaction.

Reaction conditions in the dehydration/isomerization zone in order to achieve the desired oxygen content of below 4000 ppm oxygenate, and most preferably less than 1000 ppm oxygenate, are listed below:

Condition	Broad	Preferred	Most Preferred
Product Oxygenate, ppm	< 4000	<2500	<1000
Product ratio of 2-butene to total C_4	> 0.1	> 0.5	> 0.75
Temperature, °F	> 50	50 - 900	300 - 600
Pressure, psig	> 0	> 0 - 2000	5 -250
LHSV, hr-1	> 0.01	0.1 - 10.0	1.0 - 5.0

The level of acidity of the isomerization-dehydration catalysts can be measured using the Alpha Test described in the following publications:

J. N. Miale, N. Y. Chen, and P. B. Weisz, J. Catalysis, 6, 278, (1966);

P. B. Weisz and J. N. Miale, J. Catalysis, 4, 527, (1965); and D. S. Shihabi,

W. E. Garwood, P. Chu, J. N. Miale, R. M. Lago, C. T-W. Chu, and

C. D. Chang, J. Catalysis, 93, 471, (1985). In this test, the alpha value correlates with acidity, and higher alpha values indicate stronger acids. For weakly acidic materials with alpha values below 1.0, the test can become unreliable. But with care, weakly acidic materials such as alumina have been measured reliably and found to have an alpha value of 0.7. Suitable catalytic materials for this invention should possess a minimum of acidity and have an alpha value of at least 0.7.

The feedstock to the dehydration/isomerization zone should contain a maximum of C_3-C_4 oxygenates and include the butene which is to be isomerized. Since the boiling range of the oxygenates is higher than the boiling range of the

corresponding paraffins and olefins, the following pure compound boiling ranges are relevant to selection of a suitable boiling range of the feed to the dehydration/isomerization zone. The end point of the feed for the dehydration/isomerization zone should be less than about 300°F. Preferably, the

5   boiling range is between about 15° and 250°F. This preferred range would include the butenes, which can be subjected to isomerization, but would exclude propylene. If propylene is to be alkylated and it is not in the feed to the isomerization-dehydration reactor, it can be blended with the dehydrated product and the mixture fed to the alkylation unit. Higher boiling range feeds can also be

10   dehydrated if desired for needs other than the production of olefins for alkylation. Such a situation may occur if additional higher boiling range olefins are desired for another process such as oligomerization, or the higher boiling range oxygenates are undesirable in higher boiling range products such as naphthas or distillate fuels.

15   Propanol and butanol present in other Fischer-Tropsch hydrocarbonaceous products can be added to the feed to the dehydration/isomerization zone. Propanol and butanol can be separated from other hydrocarbonaceous fractions by extraction with water followed by distillation. This would produce a stream with a concentrated amount of propanol and butanol which would then be dehydrated to

20   form olefins. Lighter boiling butenes recovered from the Fischer-Tropsch process can be blended with the propanol and butanol and processed over an isomerization-dehydration catalyst to produce a product rich in the desired 2-butene, and with an oxygenate content of less than 4000 ppm.

       Propanol and butanol will also be present in the aqueous phase that is a

25   by-product of the Fischer-Tropsch reactor. These alcohols can be separated from the water by extraction with a light hydrocarbon, such as pentane, followed by distillation. Techniques for recovery of these alcohols from an aqueous stream are well-known and described in the article "Factors Influencing Solvent Selection for Extraction of Ethanol from Aqueous Streams," Curtis Munson and C. Judson

King, I&EC Process Design and Development, 1984, Vol 23, pages 109-115. The propanol and/or butanol from any or all of these sources can be combined and fed to the dehydration/isomerization reactor.

5   Acetic and propanoic acids are possible oxygenate impurities in the feed to the dehydration/isomerization zone. They may cause corrosion and catalyst fouling and it is desirable to remove these acids. Methods to remove organic acids from hydrocarbonaceous feeds are well known and include contacting with water, preferably water that has a pH > 7.0, or by adsorption onto a solid, such as alumina, but preferably a solid that has some added alkali. Both the water washing

10   and the adsorption on a solid are performed at near ambient conditions; for example, a temperature between 50° and 200°F, and a pressure between atmospheric and 500 psig. The amount of water or solid used in these processes relative to the hydrocarbonaceous feed depends on the relative contents of acids and alcohols. Sufficient water or solid should be used to remove the acid, but not

15   the desirable alcohol. Some experimentation may be required to determine the exact proportions for a given feed composition. The acids can also be destroyed during the dehydration process or in a separate process by conventional decarboxylation. Decarboxylation is a thermal reaction (not necessarily requiring a catalyst) and can occur simultaneously with dehydration. Suitable temperatures

20   for decarboxylation are greater than 250°F, a pressure equal to or greater than atmospheric, and LHSV in the reactor of between 0.01 and 10 hr-1. The acids should be removed to the extent that they will no longer present a corrosion problem.

       The extent of acid removal can easily be evaluated by mixing one volume

25   of hydrocarbon with 0.25 volumes of water that initially has a pH from between 6.5 and 7.5. The mixture is shaken at room temperature and the water phase collected and analyzed for pH. The extent of removal of acids is sufficient if the recovered water phase from this test is greater than 4.0, preferably greater than 5.0, and most preferably between 6.0 and 8.0. The pH value of the recovered

water in this test is referred to as the acid value of the original hydrocarbon
because direct measurement of acids in hydrocarbons is difficult and not as
meaningful as a measure of the pH of the water that comes in contact with them.

  A preferred feature of the invention is to utilize a Fischer-Tropsch product
to generate the isobutane stream used in the alkylation process. The stream should
contain at least 30 wt.% isobutane, preferably at least 50 wt.%, and most
preferably, at least 75 wt.%. As mentioned previously, the C_4 stream from a
Fisher-Tropsch synthesis lacks sufficient levels of isobutane. The isobutane stream
is generated by hydrotreating and hydrocracking the 300°F+ product obtained
from the distillation zone as previously described. The 300°F+ product is
transported from the distillation zone to a hydrotreatment/hydrocracking complex.

  Hydrotreatment is a well-known technique designed to remove elemental
impurities such as sulfur and nitrogen and compounds containing sulfur, nitrogen
and oxygenates from carbonaceous products. Reaction conditions vary over a
wide range and the selection of suitable conditions would be well within the
purview of those skilled in the art. Typical hydrotreating conditions include
temperature ranges of 300°-750°F, hydrogen to oil ratios of greater than 50
SCF/Bbl and overall LHSV of greater than 0.25, preferably about 1-4.

  Effluent from the hydrotreating zone is forwarded to a distillation zone.
Recovered fractions include light gases, a naphtha fraction, a distillate fuel
fraction, a heavy hydrocarbon product and an isobutane-containing stream. The
heavy hydrocarbons are circulated to a hydrocracker. Reaction conditions to
achieve optimum hydrocracking would be within the purview of those skilled in
the art. Hydrocracking is effected by contacting the fraction or combinations of
fractions with hydrogen in the presence of a suitable catalyst at temperatures
ranging from about 600°-900°F, pressures ranging from about 200-4000 psia and
space velocities ranging from about 0.1-10 hr^{-1}. The hydrocracker effluent is then
forwarded to a distillation zone from which various boiling range fractions are
recovered, one of which is an isobutane fraction.

Alternatively, the isobutane feed can be obtained from other sources. A C_4 fraction obtained from natural gas or petroleum contains isobutane and n-butane. Since the isobutane/n-butane ratio typically is below 1, it is desirable to isomerize the C_4 paraffin fraction using conventional techniques to increase the level of

5   isobutane.

The isobutane stream is forwarded to the alkylation zone. It may be admixed with the C_3-C_4 olefin stream before entering the alkylation zone or separate streams may be circulated to the zone. As indicated earlier, alkylation of olefins with isobutane is a well-known technology and extensively described in the

10   literature as well as in many patents. Representative articles include the following: "Saga of a Discovery: Alkylation", Herman Pines, Chemtech, March 1982, pages 150-154; "The Mechanism of Alkylation of Paraffins", Louis Schmerling, Industrial and Engineering Chemistry, Feb. 1946, pages 275-281; "The Alkylation of Iso-Paraffins by Olefins in the Presence of Hydrogen Fluoride", Carl B. Linn

15   and Aristid V. Grosse, American Chemical Society, Cleveland Meeting, April 2-7, 1944; "H_2SO_4, HF Processes Compared, and New Technologies Revealed", Lyle Albright, Oil and Gas Journal, Nov. 26, 1990. U.S. Patents which disclose methods of alkylating olefins with isoparaffins include the following: 6,194,625; 5,792,896; 5,654,251.

20   Key elements of the alkylation process include contacting a mixture of an isoparaffin (usually isobutane, but isopentane can also be used either by itself or as a mixture with isobutane) with an olefin (usually propylene and butenes but also pentene) in the presence of an acid catalyst. The most frequently used acid catalysts are sulfuric and hydrofluoric acids in liquid form. The pressure of the

25   alkylation reaction using these acids should be sufficient to keep the olefins and isoparaffin in the liquid phase at reaction temperature. The reaction is exothermic, and inlet temperature are near ambient conditions. Internal cooling is commonly used to remove the heat of reaction. Sulfuric acid alkylation plants typically

operate at between 45° and 55°F and use a refrigeration system to control the heat of reaction. Hydrofluoric acid plants typically operate at between 90° and 100°F using cooling water to control the heat of reaction. The molar ratio of isoparaffin to olefin should be greater than 1.0 in order to avoid polymerization. In general, typical molar ratios are above 4 and most typically between 4 and 12. When using sulfuric acid as the alkylation catalyst, typical ratios are between 5 and 10. With hydrofluoric acid, typical ratios are between 8 and 12. Contact times in the mixer are in excess of 1 minute but typically less than 1 hour, usually 10-40 minutes. After reaction, the hydrocarbon phase which consists of the alkylation product, unreacted isobutane and smaller amounts of unreacted olefin, is separated from the acid phase by density difference. The acid is recycled to the reactor, and may be cooled during this recycle operation. The hydrocarbon products are separated by distillation to recover the high boiling, high octane, highly branched isoparaffinic product and unreacted isobutane. The unreacted isobutane is recycled to the reactor. Both H_2SO_4 and HF will react with water in the feedstock and become diluted. With sulfuric acid, no special precautions need to be taken except for a coalescer to separate entrained water from the feed. With hydrofluoric acid, the feedstock is dried by passage over an adsorbent (typically a zeolite) to reduce the water content to low values (typically below 50 ppm, preferably below 10 ppm).

The invention will now be illustrated by the following example which is intended to be merely exemplary and in no manner limiting.

EXAMPLE

The following embodiment includes the conversion of propanol and butanol in higher boiling fractions into propylene and butene which is combined with the propylene and butene obtained directly from the Fischer-Tropsch reaction. Alkylate is then made from the composite stream.

With reference to the Figure, a synthesis gas is reacted over a cobalt catalyst in a slurry bed Fischer-Tropsch reactor (10). The product from the

reaction includes a gas phase and a waxy liquid phase. The gas phase is cooled in a separation zone (20) to condense hydrocarbons. Unreacted synthesis gas which is not condensed, is recycled to the Fischer-Tropsch reactor. Water contained in the gas phase is separated from the condensed hydrocarbons by density

5   differences. The condensed hydrocarbons along with the waxy liquid are distilled in zone (30) to form a light gas product (methane and ethane), a C_3-C_4 stream that contains olefins, a C_5-300°F naphtha that also contains propanol and butanol, and a 300°F+ product. The C_3-C_4 stream is combined with the C_5-300°F naphtha and forwarded to an Dehydration/Isomerization reactor (40) containing an acidic

10   catalyst. Traces of acids in the feed are converted to non-acidic species during the Dehydration/Isomerization reaction. The conditions in the reactor (40) are 400°F (adjusted as needed to achieve a 4000 ppm maximum oxygen content), alumina-bound SSZ-32 zeolite, 1.0 LHSV, and 10 psig. The product from the Dehydration/Isomerization reactor (40) is circulated to a separation zone (50)

15   where water from the dehydration reaction is removed. A liquid hydrocarbon stream is forwarded to a distillation zone (60). A C_3-C_4 olefin-containing stream is obtained that has an oxygenate content below 1000 ppm oxygen, and a 2-butene to total butene molar ratio of > 0.3. A heavier naphtha stream is also obtained which comprises mostly the non-oxygenates in the C_5-300°F product.

20   The 300°F+ product is hydrotreated in reactor (70) to remove oxygenate and olefin impurities using a sulfided NiMo/Al$_2$O$_3$ catalyst at 1500 psig, 700°F and 1.0 LHSV and the product distilled in zone (80) to recover light gases (not shown), an isobutane-containing stream, naphtha, distillate fuel products and heavy hydrocarbons. The heavy hydrocarbons are hydrocracked in reactor (90) over a

25   sulfided NiW/SiO$_2$-Al$_2$O$_3$ catalyst at 1.0 LHSV, 1500 psig, and a temperature sufficient to achieve 60% per-pass conversion below the 5% point of the heavy hydrocarbons as determined by ASTM procedure D-2887.

     The isobutane-containing stream from the distillation unit (80) is mixed with the C_3-C_4 olefin stream recovered from the distillation unit (60). The mixture

is alkylated in reactor (100) using sulfuric acid catalyst and a high octane alkylate stream recovered. The research octane number of the alkylate is 85 and higher, preferably 90 or higher, most preferably 93 and higher. Optionally, the mixture can be blended with naphthas recovered from the Fischer-Tropsch process and/or

5   the hydrocracker (90) to produce a blend with a research octane number of 80 or higher, preferably 90 or higher. The products from the alkylation, Fischer-Tropsch and hydrocracking steps do not contain significant quantities of aromatics. Blends of these streams contain less than 10 wt% aromatics. Aromatics are undesirable in gasolines due to environmental concerns.

10   Research Octane Numbers are determined according to ASTM D2699: "Standard Test Method for Research Octane Number of Spark-Ignition Engine Fuels".

         While the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be

15   apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and the scope of the claims appended hereto.